

Nuclear Magnetic Relaxation of Molecular Reorientation in Liquid

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Molecular reorientation of oblate symmetric top molecules in the presence of internal rotation is investigated and an analytic expression for the overall reorientational correlation time is obtained. The overall reorientation of the symmetric top is treated by the anisotropic rotational diffusion and the internal rotation is analyzed by employing a model which describes jumps between several discrete states with different lifetimes. The lifetimes thus obtained can be compared with the internal angular momentum correlation time which appears when the internal rotation is treated by a modified extended rotational diffusion model.

Introduction

Study on molecular reorientation in liquid has been carried out by many workers both theoretically and experimentally. Experimental methods¹ include NMR, IR, Raman, and Rayleigh light scattering and theoretical methods² include rotational diffusion³⁻⁵, jump diffusion⁴⁻⁶, and extended rotational diffusion models^{7,8}. Of these models, the extended rotational diffusion model proposed by Gordon⁷ is known to give the best description. Other workers have applied this model to linear⁷, spherical top⁹, and symmetric top¹⁰ molecules.

Investigation of internal rotation with the extended rotational diffusion model was carried out by Spiess *et al.*¹¹ and later by Bull¹². Sometime ago we^{13,14} extended the approach of Spiess *et al.* and proposed an analytic expression for the overall reorientational correlation time in terms of the internal angular momentum correlation time which is a typical parameter involved in the extended rotational diffusion model. Comparison between the analyses for the dipole-dipole interaction¹³ and the spin-rotational interaction¹⁵, enables us to determine the internal angular momentum correlation time unambiguously.

On the other hand, the segmental motion of polymers in liquid has attracted many attention due to the exciting nature of polymers^{16,17}. Usually, one applies rotational diffusion or jump diffusion to the segmental motion which contains multiple internal rotation. London and Avitabile¹⁸ proposed a model which describes jumps between several discrete states with different lifetimes. We applied their model to interpret the relaxation rate of *n*-heptane in liquid state.¹⁹ In this model, internal rotations are assumed to be independent and as the chain length becomes longer this assumption turns out to be a rather severe one.

The purpose of this work is to apply the above model proposed by London and Avitabile to simple molecules with internal rotation such as an oblate symmetric top molecules. The independence of the internal rotation would then be a milder assumption. The internal rotation of an internal rotor such as a methyl group may be an analogy of the segmental rotation in a polymer chain and it can be described by jumps between *trans* (*t*) and *gauche* (*g*⁺, *g*⁻) states with different life times (τ_t and $\tau_g = \tau_{g^+} + \tau_{g^-}$). In this model the ratio of the lifetimes, $\sigma = \tau_t/2\tau_g$, appears as an adjustable par-

ameter. This can be related to the internal angular momentum correlation time which appears in our previous analysis with a modified version of the extended internal rotational diffusion model.

When there is no internal rotation it is not necessary to distinguish prolate symmetric tops from oblate symmetric top molecules in the theoretical formulation of molecular reorientation. Existing theories describing internal rotation are dealing implicitly with prolate symmetric top mainbody. Our previous work¹⁴ was also in the same spirit and toluene molecule was assumed to be a prolate symmetric top molecule. However, when the internal rotor is attached to an oblate symmetric top molecule such as mesitylene the situation becomes quite different since the axis of internal rotation is along the minor principal axis of the mainbody. Previous theories are applicable to the case when the axis of internal rotation is along the major principal axis of the prolate symmetric top mainbody.

Theory

The overall reorientational correlation function in the presence of internal rotation is given by⁸

$$G_{jklm}(t) = \frac{\langle D_{jk}^{(2)}[\Omega_{LF}(0)] D_{lm}^{(2)*}[\Omega_{LF}(t)] \rangle}{\langle D_{jk}^{(2)}[\Omega_{LF}(0)] D_{lm}^{(2)*}[\Omega_{LF}(0)] \rangle} \quad (1)$$

where $D_{jk}^{(2)}$ is the second rank Wigner rotation matrix element¹⁴ and Ω_{LF} is the Euler angles connecting the laboratory fixed coordinate system and the coordinate system fixed to the internal rotor. $\langle \dots \rangle$ denote the ensemble average. Here we are considering an oblate symmetric top molecule with internal rotation about a minor principal axis of the mainbody which is the axis of tumbling reorientation. The major principal axis is taken to be the z-axis of the principal coordinate system fixed to the mainbody. The rotation matrix element can be further decomposed into

$$D_{lm}^{(2)}[\Omega_{LF}] = \sum_k D_{lk}^{(2)}[\Omega_{LD}] D_{kl}^{(2)}[0, \pi/2, 0] D_{jm}^{(2)}[\alpha, \beta, 0] \quad (2)$$

where the summation is from -2 to $+2$ and Ω_{LD} is the Euler angles connecting the laboratory fixed frame and the principal coordinate system. The second set of Euler angles represents the transformation from the principal coordinate system to the coordinate system fixed to the mainbody with

the z -axis coincident with the minor principal axis. The last set of Euler angles are required to transform to the coordinate system fixed to the internal rotor such as a methyl group. In this case the z -axis is taken to be along the C-H bond and β is the fixed tetrahedral angle and γ is set to zero without loss of generality. The angle α is the time-dependent internal rotation angle.

The numerator of Eq. (1) then becomes

$$\begin{aligned} & \langle D_{jk}^{(2)}[\Omega_{LF}(0)] D_{lm}^{(2)*}[\Omega_{LF}(t)] \rangle \\ &= \sum_{a,b,c,d} \langle D_{ja}^{(2)}[\Omega_{LD}(0)] D_{lb}^{(2)*}[\Omega_{LD}(t)] D_{ac}^{(2)}[0, \pi/2, 0] \\ & \quad \times D_{bd}^{(2)*}[0, \pi/2, 0] D_{cd}^{(2)}[\alpha(t), \beta, 0] D_{dm}^{(2)*}[\alpha(t), \beta, 0] \rangle \quad (3) \\ &\cong \sum_{a,b,c,d} \langle D_{ja}^{(2)}[\Omega_{LD}(0)] D_{lb}^{(2)*}[\Omega_{LD}(t)] \rangle \langle e^{-i\alpha(t)+i\alpha(0)} \rangle \\ & \quad \times d_{ac}^{(2)}(\pi/2) d_{bd}^{(2)}(\pi/2) d_{cd}^{(2)}(\beta) d_{dm}^{(2)*}(\beta). \end{aligned}$$

The second approximate equality is introduced by assuming that the overall reorientation is independent of the internal rotation. Since the reorientation of bulky mainbody may be reasonably assumed to undergo rotational diffusion, the first ensemble average becomes⁴

$$\langle D_{ja}^{(2)}[\Omega_{LD}(0)] D_{lb}^{(2)*}[\Omega_{LD}(t)] \rangle = \frac{1}{5} e^{-E_a t} \delta_{jl} \delta_{ab} \quad (4)$$

where

$$E_a \equiv 6D_2 + (D_1 - D_2) a^2$$

and δ_{ij} is the Kronecker delta. D_1 is the rotational diffusion constant for the spinning about the major principal axis and D_2 is for the tumbling about the minor principal axis.

The second ensemble average which represents the internal rotation is now treated by the model proposed by London and Avitabile¹⁸. Internal rotation of a side group relative to the mainbody of the molecule may be described by jumps between *trans* (t) and *gauche* (g^+ or g^-) states and the probabilities of being in each one of them can be obtained from a simple set of decay equations in the steady state approximation. It is also assumed that *gauche* states can make transitions only to *trans* states. The resulting expressions for these probabilities are

$$p(t) = (1 + 2\sigma)^{-1}, \quad p(g^+) = p(g^-) = \sigma(1 + 2\sigma)^{-1} \quad (5)$$

These probabilities together with the conditional probabilities of moving from one state to another are necessary to evaluate the ensemble average for the internal rotation to give

$$\langle \exp i[d\alpha(t) - c\alpha(0)] \rangle = \sigma(1 + 2\sigma)^2 A_{ca}(t) \delta_{ca} \quad (6)$$

where the $A(t)$ matrix is given by London and Avitabile.

Substituting Eqs. (3), (4), and (6), Eq. (1) becomes

$$\begin{aligned} G_{ik,lm}(t) &= \sum_{a,b} [d_{ab}^{(2)}(\pi/2)]^2 d_{ik}^{(2)}(\beta) d_{lm}^{(2)*}(\beta) \\ & \quad \times \exp(-E_a t) A_{ca}(t) \delta_{ij} \end{aligned} \quad (7)$$

Since the overall reorientational correlation time τ_c , which can be evaluated from NMR dipolar relaxation experiment, is defined by a time integral of $G_{\alpha\alpha, \beta\beta}(t)$ component⁴, τ_c becomes

$$\tau_c = \sum_{a,b} [d_{ab}^{(2)}(\pi/2) d_{bc}^{(2)}(\beta)]^2 \int_0^\infty dt A_{aa}(t) \exp(-E_a t) \quad (8)$$

where

$$\begin{aligned} A_{00}(t) &= (2\sigma + 1)^2 / \sigma \\ A_{11}(t) &= A_{-1,-1}(t) = A_{22}(t) = A_{-2,-2}(t) \\ &= 1/\sigma + \sigma - 2 + (9/2) \exp(-t/\tau_g) \\ & \quad + \frac{3}{2}(1 + 2\sigma) \exp(-t/\tau_g) \end{aligned} \quad (9)$$

Presence of $d^{(2)}$ matrix elements with argument $\pi/2$ simplifies Eq. (8) further to give

$$\begin{aligned} \tau_c &= \frac{1}{4}(3A + 2B + C/2) \int_0^\infty dt A_{11}(t) \exp(-E_a t) \\ & \quad + \frac{1}{2}(B + C) \int_0^\infty dt A_{11}(t) \exp(-E_a t) \\ & \quad + \frac{1}{4}(A + 3C) \int_0^\infty dt A_{00}(t) \exp(-E_a t) \end{aligned} \quad (10)$$

where $A \equiv [d_{00}^{(2)}(\beta)]^2 = \frac{1}{4}(3 \cos^2\beta - 1)^2$

$$B/2 \equiv [d_{10}^{(2)}(\beta)]^2 = \frac{3}{2} \cos^2\beta \sin^2\beta$$

$$C/2 \equiv [d_{20}^{(2)}(\beta)]^2 = \frac{3}{8} \sin^4\beta \quad (11)$$

according to Rose's formula²⁰. Integrals in Eq. (10) can be easily evaluated and the result becomes

$$\begin{aligned} \tau_c &= \frac{1}{4} A_{00} (A + 3C) (6D_2)^{-1} + \frac{a}{4} (3A + 2B + C/2) (4D_1 + 2D_2)^{-1} \\ & \quad + \frac{1}{4} (b + a/2) (3A + 2B + C/2) (4D_1 + 2D_2 + 1/\tau_g)^{-1} \\ & \quad + \frac{a}{2} (B + C) (D_1 + 5D_2)^{-1} \\ & \quad + \frac{1}{2} (b + 9/2) (B + C) (D_1 + 5D_2 + 1/\tau_g)^{-1} \end{aligned} \quad (12)$$

where

$$\begin{aligned} a &\equiv 1/\sigma + \sigma - 2 \\ b &\equiv 3/2 (1 + 2\sigma). \end{aligned}$$

It is interesting to notice that Eq. (12) can be further simplified when the ratio of lifetimes, σ , becomes 1. Then

$$\begin{aligned} \tau_c &= \frac{9}{4} (A + 3C) (6D_2)^{-1} \\ & \quad + \frac{9}{4} (3A + 2B + C/2) (4D_1 + 2D_2 + 1/\tau_g)^{-1} \\ & \quad + \frac{9}{2} (B + C) (D_1 + 5D_2 + 1/\tau_g)^{-1} \end{aligned} \quad (13)$$

The result obtained in Eq. (13) can now be compared with our previous result²¹ which employs an extended rotational diffusion model for the internal rotation:

$$\begin{aligned} \tau_c^* &= \tau_g^* \left[\frac{1}{4} F(0, 0) + \frac{3}{4} F(2, 0) + F(1, 1) + F(2, 1) \right. \\ & \quad \left. + \frac{3}{4} F(0, 2) + F(1, 2) + \frac{1}{4} F(2, 2) \right] \end{aligned} \quad (14)$$

where

$$F(a, b) = [d_{\alpha}^{(2)}(\beta)]^2 Y(a, b) [\tau_g^* - Y(a, b)]^{-1} \quad (15)$$

$$Y(a, b) \equiv \frac{1}{|b|} \sqrt{\pi/2} \exp[(E_a^* + 1/\tau_g^*)^2 / 2b^2] \\ \times \operatorname{erfc}[(E_a^* + 1/\tau_g^*) / \sqrt{2} b] \quad (16)$$

with

$$E_a^* \equiv 6D_2^* + (D_1^* - D_2^*)a^2 \\ \tau^* \equiv (k_B T / I_a)^{1/2} \tau, \quad D^* \equiv (U_a / k_B T)^{1/2} D$$

The internal angular momentum correlation time, τ_i , can be evaluated from the experimental value of the dipolar relaxation rate *via* Eq. (14) and this gives the measure of the degree of inertial effect for the internal rotation. From Eq. (13) we can also evaluate the lifetime of the gauche state. Since we assumed that $\sigma=1$ we also know that $\tau_g=2\tau_i$. Therefore, we can establish a correlation between the degree of inertial effect of the internal rotation and the lifetimes of different states.

Discussion

Description of internal rotation depends on the choice of theoretical models and the molecular geometry. For symmetric top molecules, rotational diffusion, jump diffusion, and extended rotational diffusion models are widely adopted. A different model proposed by London and Avitabile describes jumps between several discrete states with different lifetimes. This model is proposed for the segmental motion of polymers. However it can also be applied to simple molecules whenever the molecular geometry is suitable for the analysis of its internal rotation.

When the ratio of lifetimes is different from unity we have to use Eq. (12) which contains two parameters, namely, σ and τ_g . In this case, another relation is necessary and it can be provided by investigating the spin-rotational relaxation process and the work is being carried out in this direction in our group.

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